日本材料学会
塑性工学部門委員会
材料データベース研究分科会

2008年09月26日(金)

# ステンレス鋼FAモードのフェーズフィールドモデル解析

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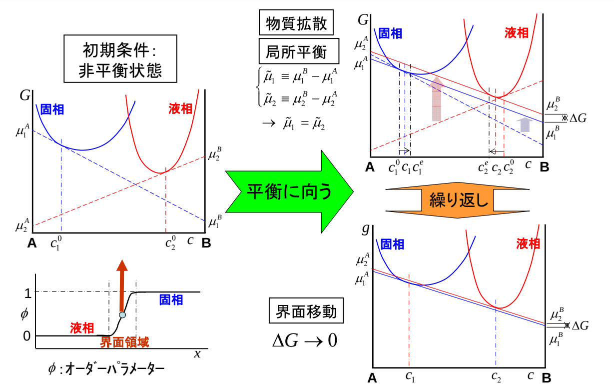
伊藤忠テクノソリューションズ株式会社

## フェーズフィールドモデルのしくみ






## 背景

◆ マルチフェーズフィールドモデル

多元系・多相系に対する理論と手法の発展

ACCESS(アーヘン工科大)
Steinbach (現、Rulr大)ら

◆ **計算状態図(CALPHAD)**

モデルと材料データベースの充実と信頼性の向上

代表的ソフトウエア
Thermo-Calc®

実用合金材料の組織形成シミュレーションへの機運が高まる

'90台後半からSteinbachらによりMICRESS® (MICRostructure Evolution Simulation Software)の開発がスタート、'05より日本での取り扱いを開始



## 本計算で用いるﾌｪｰｽﾞﾌｨｰﾙﾄﾞﾓﾃﾞﾙ方程式

◆ '90年代初等に提案された一般的なフェーズフィールドモデルが基本

① 系の自由エネルギーの定義:Ginzburg-Landau形式

$$F(\phi)=\int_V\left[\frac{\varepsilon^2}{2}|\nabla\phi|^2+f(\phi)\right]dV \qquad \begin{cases}\phi=0 & :液相\\ \phi=1 & :固相\end{cases}$$

$$\begin{cases} f(\phi)=W g(\phi)+f_2 h(\phi)+f_1[1-h(\phi)] \\ g(\phi)=\phi(1-\phi), \quad 0\le\phi\le 1 \end{cases}$$

② Allen-Cahn形式

$$\frac{1}{M}\cdot\frac{\partial\phi}{\partial t}=-\frac{\delta F}{\delta\phi}$$

**界面プロファイル**

$$h(\phi)\equiv\phi=\frac{1}{2}\sin\left(\frac{\sqrt{2W}}{\varepsilon}x\right)+\frac{1}{2}$$

$$\frac{1}{M}\frac{\partial\phi}{\partial t}=\sigma\left\{\nabla^2\phi+\frac{\pi^2}{2\delta^2}(2\phi-1)\right\}+\frac{\pi}{\delta}\sqrt{\phi(1-\phi)}\cdot\Delta G$$

ﾌｪｰｽﾞﾌｨｰﾙﾄﾞﾓﾃﾞﾙﾊﾟﾗﾒｰﾀ

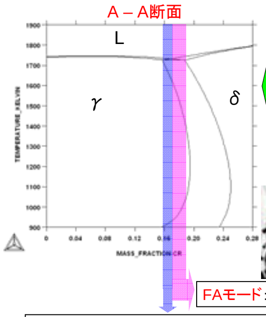
$\delta$: 界面厚み
$M$: 界面モビリティ
$\sigma$: 界面エネルギー

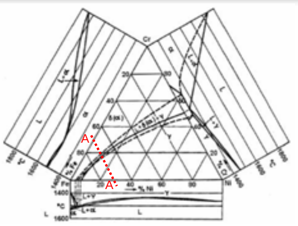


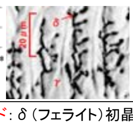
## Fe-Cr-Ni系の状態図と凝固モードの特徴

(Cr+Ni)28wt%一定

A－A断面



FAモードのバーミキュラー状残留δ組織

井上裕滋, 小関敏彦:溶接プロセスを用いたオーステナイト系ステンレス鋼の凝固形態および凝固形成機構の解明, 新日鉄技報, No.385, pp.56-63, 2006

FAモード: δ(フェライト)初晶→γ(オーステナイト)析出

AFモード: γ(オーステナイト)初晶→δ(フェライト)析出



## マルチフェーズフィールドモデル方程式

2相系:

$$\frac{1}{M}\frac{\partial\phi}{\partial t}=\sigma\left\{\nabla^2\phi+\frac{\pi^2}{2\delta^2}(2\phi-1)\right\}+\frac{\pi}{\delta}\sqrt{\phi(1-\phi)}\cdot\Delta G$$

多相系に拡張

$$\frac{\partial\phi_\alpha}{\partial t}=\sum_{\beta=1}^{\nu}M_{\alpha\beta}\left[\sigma_{\alpha\beta}\left(\phi_\alpha\nabla^2\phi_\beta-\phi_\beta\nabla^2\phi_\alpha+\frac{\pi^2}{2\delta^2}(\phi_\alpha-\phi_\beta)\right)+\frac{\pi}{\delta}\sqrt{\phi_\alpha\phi_\beta}\cdot\Delta G\right],$$

ただし、

$$0\le\phi_1,\phi_2,\cdots,\phi_\alpha,\cdots,\phi_\beta,\cdots\phi_\nu\le 1,$$

$$\sum_{\beta=1}^{\nu}\phi_\beta=1$$

## 拡散方程式と局所平衡の計算式

◆ 拡散方程式

$$\dot{\vec{c}} = V_m \nabla\left(\sum_{\alpha=1}^{2}\phi_\alpha \mathbf{M}_\alpha(\vec{c}_\alpha)\bullet\nabla\vec{\tilde{\mu}}_\alpha\right)$$

$$\dot{\vec{c}} = \nabla\left(\sum_{\alpha=1}^{2}\phi_\alpha \mathbf{D}_\alpha \bullet\nabla\vec{c}_\alpha\right),\quad \mathbf{D}_\alpha = V_m \mathbf{M}_\alpha \mathbf{T}_\alpha,\quad T^{ij} = \frac{\partial\tilde{\mu}^i_\alpha}{\partial c^j_\alpha}$$

相互拡散モビリティデータ

CALPHADデータベース

熱力データより算出

◆ 局所平衡条件

$$\begin{cases} \vec{c}_\alpha - \vec{c}^*_\alpha = \mathbf{K}_{\alpha\rho}\left(\vec{c}_\rho - \vec{c}^*_\rho\right) + \left(\dfrac{\partial c^i_\alpha}{\partial T}\right)\Delta T, \quad \mathbf{K}_{\alpha\rho} = K^{ij}_{\alpha\rho} = \left(\dfrac{\partial c^i_\alpha}{\partial c^j_\rho}\right) \simeq \mathbf{T}^{-1}_\alpha \mathbf{T}_\rho \\ \vec{c} = \sum_{\alpha=1}^{2}\phi_\alpha \vec{c}_\alpha \end{cases}$$

：分配係数 ← $\vec{\tilde{\mu}}_\alpha = \vec{\tilde{\mu}}$

$$c^i_\alpha = \frac{c^i - \sum_{\rho=1}^{\nu}\phi_\rho\left[\vec{c}^{i*}_\rho - K^{ii}_{\rho\alpha}c^{i*}_\alpha + \left(\dfrac{\partial c^i_\rho}{\partial T}\right)\Delta T\right]}{\sum_{\rho=1}^{\nu}\phi_\rho K^{ii}_{\rho\alpha}}$$

収束計算 →

$c^{i\,*}_\alpha$ ：各タイムステップ収束値

$$\Delta G_{\alpha\beta} = \Delta G^*_{\alpha\beta} + \sum_{\gamma=1}^{2}\left(\frac{\partial\Delta G_{\alpha\beta}}{\partial c^i_\alpha}\right)_{c^{i\neq j}_\beta,T}\Delta c^j_\beta + \left(\frac{\partial\Delta G_{\alpha\beta}}{\partial T}\right)_{c_\beta}\Delta T$$



## 計算条件（FAモード）－１

◆ 組成　　Fe – 18wt%Cr – 10wt%Ni

◆ Thermo-calcデータベース

TCFE4、MOB2

◆ 計算格子（二次元）

格子幅：Δx=Δy =0.25μm,

格子数：(360,1500),

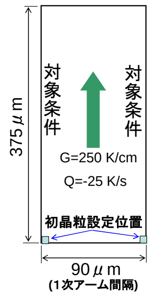
計算領域：(90,375)μm

◆ 冷却条件　G=250 K/cm,　Q=-25 K/s

◆ ﾌｪｰｽﾞﾌｨｰﾙﾄﾞ界面厚み　　4格子

◆ 初晶δ粒設定条件

(0&90μm,0)にて1格子幅の初期粒子を設定






## 熱力学モデル＆データの援用

◆ Fe-Ni-Cr熱力モデルとデータ( Thermo-Calc®)

★準正則溶体モデル

$$G^\alpha = G^\alpha_{\mathrm{Fe}}x_{\mathrm{Fe}} + G^\alpha_{\mathrm{Cr}}x_{\mathrm{Cr}} + G^\alpha_{\mathrm{Ni}}x_{\mathrm{Ni}} + L^\alpha_{\mathrm{Fe,Cr,Ni}}(x_{\mathrm{Fe}}, x_{\mathrm{Cr}}, x_{\mathrm{Ni}}, T)x_{\mathrm{Fe}}x_{\mathrm{Cr}}x_{\mathrm{Ni}}$$
$$+ L^\alpha_{\mathrm{Fe,Cr}}(x_{\mathrm{Fe}}, x_{\mathrm{Cr}}, x_{\mathrm{Ni}}, T)x_{\mathrm{Fe}}x_{\mathrm{Cr}} + L^\alpha_{\mathrm{Fe,Ni}}(x_{\mathrm{Fe}}, x_{\mathrm{Cr}}, x_{\mathrm{Ni}}, T)x_{\mathrm{Fe}}x_{\mathrm{Ni}} + L^\alpha_{\mathrm{Ni,Cr}}(x_{\mathrm{Fe}}, x_{\mathrm{Cr}}, x_{\mathrm{Ni}}, T)x_{\mathrm{Ni}}x_{\mathrm{Cr}}$$
$$+ RT\left[y_{\mathrm{Fe}}\ln y_{\mathrm{Fe}} + y_{\mathrm{Cr}}\ln y_{\mathrm{Cr}} + y_{\mathrm{Ni}}\ln y_{\mathrm{Ni}}\right],\quad \alpha = \text{Liquid, FCC, BCC}$$

★熱力データ

$G^\alpha_{\mathrm{Fe}},\ G^\alpha_{\mathrm{Cr}},\ G^\alpha_{\mathrm{Ni}},\ L^\alpha_{\mathrm{Fe,Cr,Ni}},\ L^\alpha_{\mathrm{Fe,Cr}},\ L^\alpha_{\mathrm{Fe,Ni}},\ L^\alpha_{\mathrm{Ni,Cr}},\quad \alpha = \text{Liquid, FCC, BCC}$

★拡散モビリティデータ

$M_{i,j},\quad i, j = \text{Fe, Cr, Ni}$

TQ-Interface

マルチフェーズフィールドモデルプログラム　(MICRESS®)



## 計算条件（FAモード）－２

◆ 界面エネルギー　　$\sigma(\theta) = \bar{\sigma}\left[1 + \varepsilon_4\cos(4\theta)\right]$

$\sigma_{L\text{-}\gamma} = \sigma_{L\text{-}\delta} = 2\times10^{-5}$ J/cm², $\varepsilon_4$=0.011

$\sigma_{\gamma\text{-}\delta} = 7\times10^{-5}$ J/cm²,

$\sigma_{\gamma\text{-}\gamma} = 4\times10^{-5}$ J/cm², $\varepsilon_4$=0.011

◆ 界面モビリティ　　$K(\theta) = \bar{K}\left[1 + \varepsilon_4\cos(4\theta)\right]$

$K_{L\text{-}\gamma} = K_{L\text{-}\delta} = 5\times10^{-2}$ cm⁴ /J/s, $\varepsilon_4$=0.011

$K_{\gamma\text{-}\delta} = 1\times10^{-4}$ cm⁴ /J/s

$K_{\gamma\text{-}\gamma} = 3\times10^{-3}$ cm⁴ /J/s, $\varepsilon_4$=0.011

◆ γ核生成条件　生成位置：液相-γ界面

最小過冷度：1.0K

生成最大温度：1728K (1455C)

生成判別時間間隔：0.01Sec.

生成核間最小距離：1.5μm

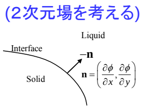
生成核結晶方位分布：-5～+5Deg （対初晶結晶方位）



## 異方性の与え方とパラメータ

◆ 異方性のフェーズフィールドモデル：(2次元場を考える)

$$\sigma = \sigma(\theta),\qquad \tan\theta = \frac{\partial\phi/\partial y}{\partial\phi/\partial x} \equiv \frac{\phi_y}{\phi_x}$$




$$\mathbf{n} = \left(\frac{\partial\phi}{\partial x}, \frac{\partial\phi}{\partial y}\right)$$

$$\delta F = \int_V\left[\delta f + \delta\left(\frac{\varepsilon^2}{2}(\nabla\phi)^2\right)\right]dV = \int_V\left[\delta f + (\nabla\phi)^2\sigma\delta\sigma + \sigma^2\nabla\phi\cdot\nabla\delta\phi\right]dV$$

$$\frac{1}{M}\frac{\partial\phi}{\partial t} = -\frac{\delta F}{\delta\phi}$$

$$\frac{1}{M}\frac{\partial\phi}{\partial t} = \sigma^2\nabla^2\phi - \frac{\partial f}{\partial\phi}$$
$$+\sigma\sigma'\left[2\cdot\cos(2\theta)\cdot\phi_{xy} + \sin(2\theta)\cdot(\phi_{yy} - \phi_{xx})\right] - \frac{1}{2}\left(\sigma'^2 + \sigma\sigma''\right)\left[2\cdot\sin(2\theta)\cdot\phi_{xy} - \nabla^2\phi - \cos(2\theta)\cdot(\phi_{yy} - \phi_{xx})\right]$$

$\sigma' \equiv \partial\sigma/\partial\theta,\ \sigma'' \equiv \partial^2\sigma/\partial\theta^2,\ \phi_{xx} \equiv \partial^2\phi/\partial x^2,\ \phi_{yy} \equiv \partial^2\phi/\partial y^2,\ \phi_{xy} \equiv \partial^2\phi/\partial x\partial y$

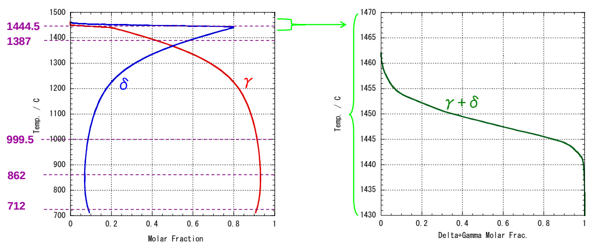
◆ 異方性パラメータの定義

平衡形の1つの解：$\sigma(\theta) = \bar{\sigma}\left[1 + \varepsilon^\sigma_4\cos(4\theta)\right]$　同一形を適用 →　$M(\theta) = \bar{M}\left[1 + \varepsilon^M_4\cos(4\theta)\right]$

界面ｴﾈﾙｷﾞｰの異方性係数　　界面ﾓﾋﾞﾘﾃｨの異方性係数



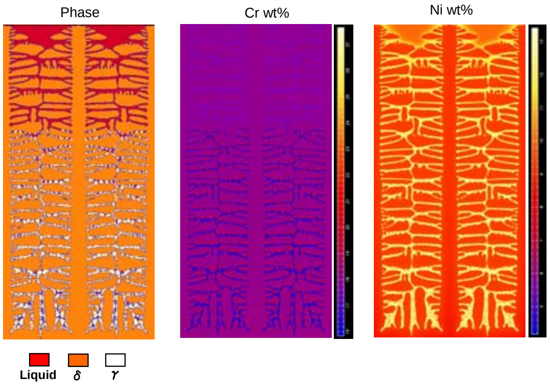
## 計算結果（FAモード）：δとγのモル分率変化




| Mol-frac. \ ℃ | 1444.5 | 1387 | 999.5 | 862 | 712 |
|---|---|---|---|---|---|
| δ | 76.9% | 56.9% | 8.5% | 6.9% | 9.3% |
| γ | 12.2% | 43.1% | 91.5% | 93.1% | 90.7% |

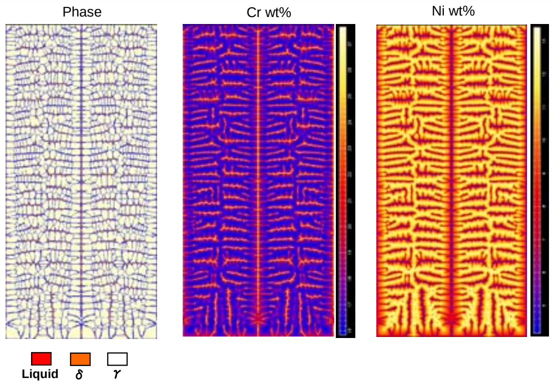
実験値：5～10%

## 1444.5℃ (0.7 sec.)での相＆組成分布



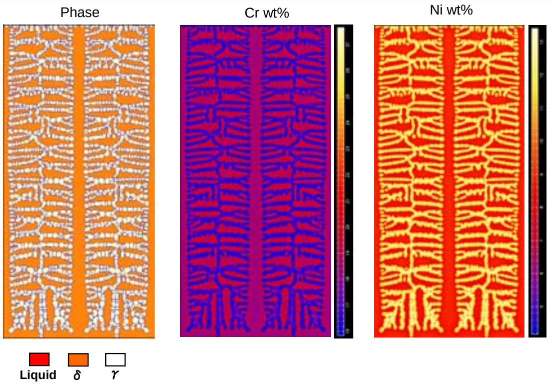



## 712℃ (30 sec.)での相＆組成分布






## 1387℃ (3.0 sec.)での相＆組成分布



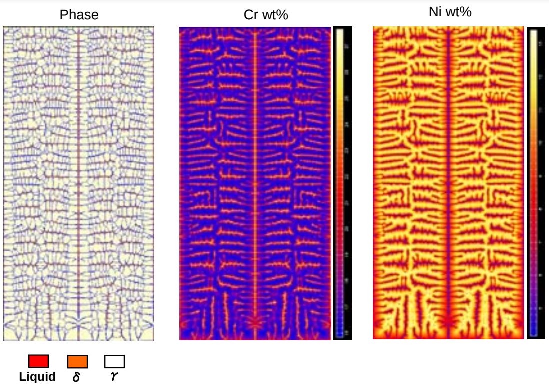



## まとめ

多元系多相系熱力学データベースを連携させたマルチフェーズフィールドモデルと相互拡散方程式および局所平衡条件の連成計算により、合金凝固組織計算が良好に実施されることを、ステンレス鋼のFAモード凝固計算を通じて確認した。



## 999.5℃ (18.5 sec.)での相＆組成分布



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# *Al合金凝固組織形成のフェーズフィールドモデル解析*

*Numerical simulation for grain refinement of aluminum alloy by Multi-phase-field model associated with CALPHAD*
*2008.09.24　鉄鋼協会秋季講演大会にて発表*

野本 祐春

## *Contents*

- *Introduction: Background and Aims*
- *Calculation method*
- *Al-Ti alloys containing TiB2 particles*
- *Al-2wt%Si-Ti alloys containing 0.12wt%TiB2 particles*
- *Conclusion*

19

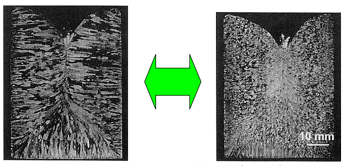
## *Basic technique for refinement*

- The grain refinement of aluminum alloys which can be achieved by the addition of master alloys to the melt has been an important technique, *inoculation*, for improving mechanical properties.
- The most widely used master alloys for α-Al are based on some compounds of Al-Ti-B, in which $TiB_2$ particles work as an effective refiner.

[97Spittle][99Lee]

20

## *Refinement mechanism*




0.03wt%$TiB_2$ added 0.03wt%$TiB_2$ and 0.01wt%Ti added

1) M.Easton and D.StJohn, Metallurgical and Materials Trans., 30A(1999), 1625-1633

- The main factors for grain size refinement are not only the density and radius distribution of $TiB_2$ particles, but also the Ti content. [99Lee] *etc.*
- The growth restriction factor [*GRF*] is a parameter of the strength of the refinement effect.
- $GRF=m_L(k-1)C_0$

21

So far…

- Some models describing the refining mechanism have been proposed. [99Easton] [04,05Quested]
- Cellular-automaton has been applied to simulate the refinement in solidification of Al alloys [1] .
- It has been proposed that the multi-phase field model using Seed Density Model, radius and density distributions of nuclei, is valuable to simulate the refinement for equiaxed solidification of Al alloy[2] .

[1] H.W.Hongwei and K.Nakajima, will be published
[2] B.Boettger, J.Eiken and I.Steinbach, Acta Mater., 54(2006) 2697-2704

22

## *Aims of this study*

- We will rigorously confirm that the grain sizes for equiaxed solidification of Al alloy calculated by the multi-phase field model[1] coupled with CALPHAD[2] and by using calibrated seed density model data are in agreement with experimental measurements in various Ti contents.

1) http://www.micress.de/
2) http://www.thermocalc.com/index.html

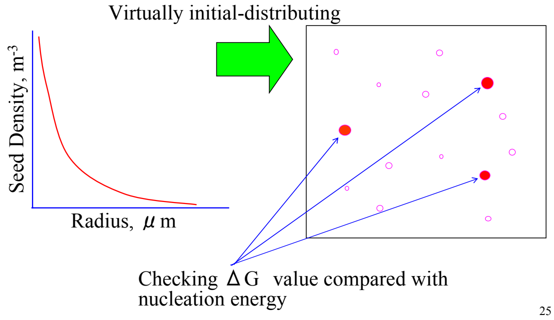
23

## *Seed Density model*

B.Boettger, J.Eiken and I.Steinbach, Acta Mater., 54(2006) 2697-2704

24

## *Distribution of Seed Density model*

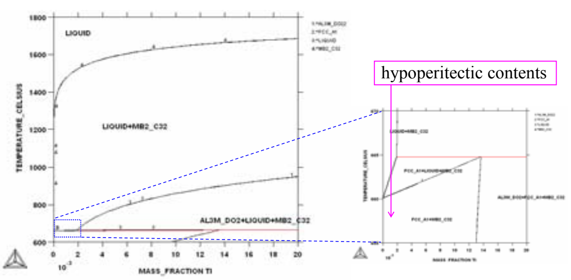





## *Calculation for Al-Ti alloys containing $TiB_2$ particles*



## *Quasi-phase diagram of* Al-Ti *system* (0.03wt%B)




- $TiB_2$ phase is steady at temperatures higher than 665℃
- $TiB_2$ particle is a good nucleant for $\alpha$-Al [99Easton][02Murty]

## *Calculation conditions*

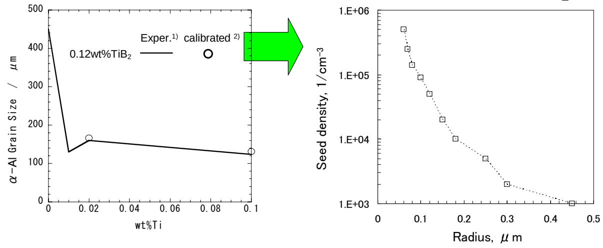
- Area size: (600 μm,600 μm)
- Grid size: 2.0 μm
- Interfacial energy[J/m²]: $\sigma_{FCC\text{-}L}$=0.1 [88T.Lida&R.L.Guthrie] [06K.Nakajima]
- Diffusivity [m²/s ]: $D_{Ti}^{L}= 5\times10^{-9}$ [88T.Lida&R.L.Guthrie]
  $D_{Ti}^{FCC}$ ← Diffusion Database "MOB2"
- Latent heat [J/m³]: $H_{FCC}=1.08\times10^{9}$
- Specific heat [J/m³/K ]: $Cp_L=2.6\times10^{6}$、$Cp_{FCC}=2.5\times10^{6}$

  } JSME Databook
- Interface mobility[m⁴ /J/s ]: $M_{FCC\text{-}L}=5\times10^{-10}$ T>931K,
  $M_{FCC\text{-}L}=5\times10^{-12}$ T=<931K
- Heat extraction ratio[J/s/m³]: $50\times10^{6}$



## *Calibration of seed density and radius for $\alpha$-Al nucleus size of equiaxed solidification*

- Seed model A: 0.12wt%$TiB_2$




- Min. nucleation temperature : 932 K

1) M.Easton and D.StJohn, Metallurgical and Materials Trans., 30A(1999), 1625-1633
2) B.Boettger, J.Eiken and I.Steibach, Acta Mater., 54(2006) 2697-2704



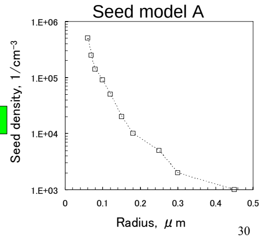
## *Seed Model B for* 0.03wt%$TiB_2$

### *Assumption*

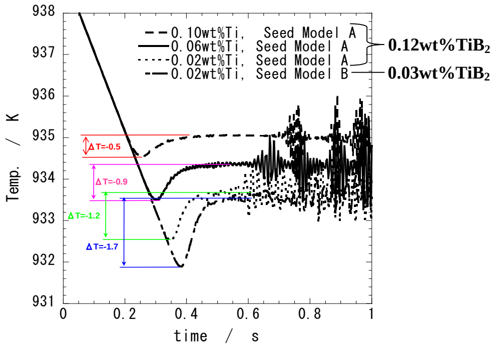
- Radius distribution of inoculants is constant regardless of $TiB_2$ content

Number of particles in seed model B = 1/4 × that of model A

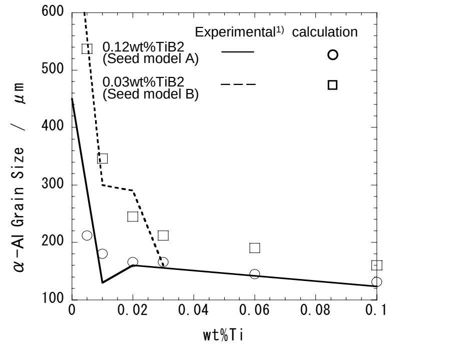
Seed model A



## *Cooling curves with variations of Ti contents and additions of 0.12 and 0.03wt%$TiB_2$*



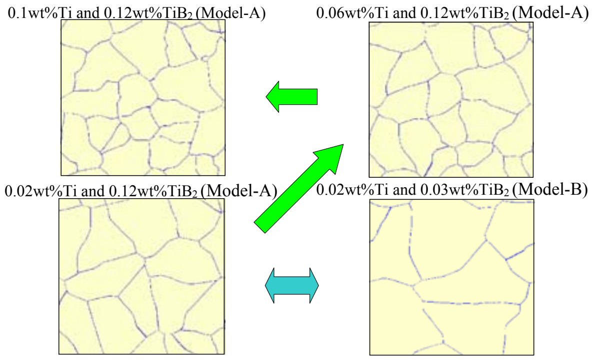

## *Grain size with variation of Ti contents on additions of 0.12 and 0.03wt%$TiB_2$*



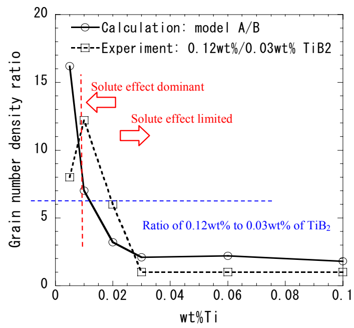

1) M.Easton and D.StJohn, Metallurgical and Materials Trans., 30A(1999), 1625-1633



## *α-Al grain distributions with variations of Ti contents and additions of 0.12 and 0.03wt%$TiB_2$*

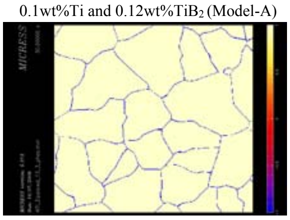



## *Solute effect for refinement*

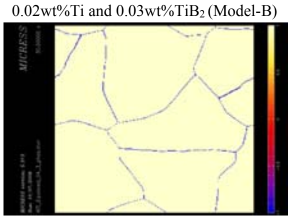



## *Animations of α-Al grain distributions*

0.1wt%Ti and 0.12wt%$TiB_2$ (Model-A)



0.02wt%Ti and 0.03wt%$TiB_2$ (Model-B)



# *Calculation for Al-2wt%Si-Ti alloys containing 0.12wt%$TiB_2$ particles*

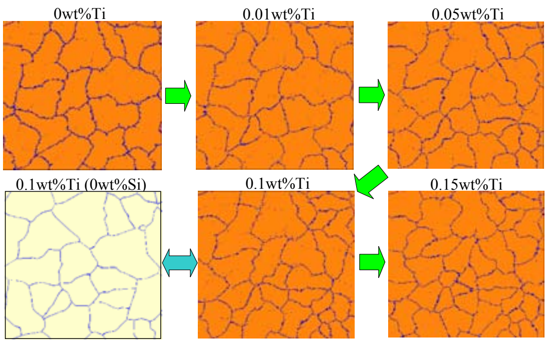
# Calculation conditions

・Area size: (600 μm, 600 μm)
・Grid size: 2.0 μm
・Seed density model for α-Al nuclei: Model-A
(assuming as same as Al-Ti- B Case)
・Interfacial energy[J/m$^2$]: $\sigma_{Si\text{-}L}$=10.0 [1)]
・Diffusivity [m$^2$/s ]: $D_{Si}^{L}$= 5×10$^{-9}$ [88T.Lida&R.L.Guthrie]
$D_{Si}^{FCC}$ ← Diffusion Database "MOB2"
・Latent heat [J/m$^3$]: $H_{Si}$=1.16×10$^9$ } JSME Databook
・Specific heat [J/m$^3$/K ]: $Cp_{Si}$ =2.31×10$^6$ } JSME Databook
・Interface mobility[m$^4$ /J/s ]: $M_{Si\text{-}L}$=1×10$^{-13}$
Other values were the same as the previous case

[1] B.Boettger, J.Eiken and I.Steibach, Acta Mater., 54(2006) 2697-2704

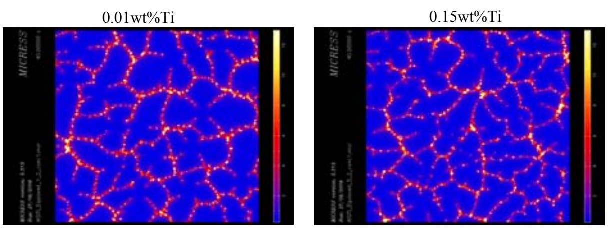


## α-Al and Si grain distributions with variations of Ti contents



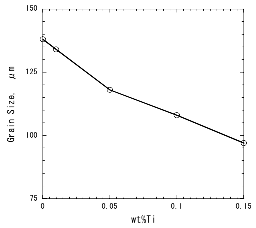



## Animation of Si wt% distribution






## α-Al grain size with variations of Ti contents




Tendency for grain size to decrease with increase of solute-Ti increasing is in qualitative agreement with experimental mesurements[1)]. However, the experimental data in constant $TiB_2$ content is more necessary to calibrate seed density.

[1] Y.C.Lee *et.al.*, Material Science and Engineering A259(1999) 43-52



# Conclusion

- It has been confirmed that the multi-phase field model working with CALPHAD databeses can be an effective tool to simulate equiaxed solidification of Al alloys.
- It is important for quantitative simulation to obtain the seed density data by calibration comparing with solidification experiments.



# Conclusion

- It has been confirmed that the multi-phase field model working with CALPHAD databeses can be an effective tool to simulate equiaxed solidification of Al alloys.
- It is important for quantitative simulation to obtain the seed density data by calibration comparing with solidification experiments.